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Improvement in Preparation and Properties

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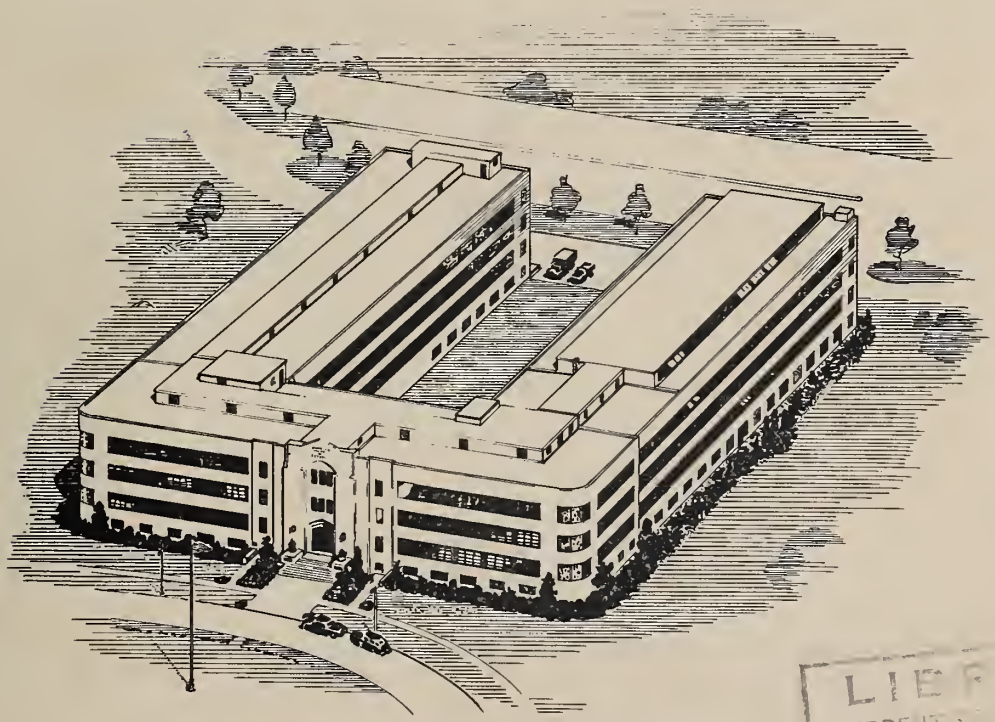

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Methods of preparation and various formulations of allyl starch emulsions have been described by Wrigley, Schwartz, and Siciliano.[1/] Practical tests of these emulsions brought forth a number of suggestions for modifications, particularly to increase the hardness of the films and to provide for varying the viscosity of the emulsions. This paper describes attempts to increase the rate of hardening of allyl starch emulsion films by decreasing the amount of plasticizer or emulsifier, or both, or by adding cobalt complexes as polymerization catalysts. Certain other modified techniques and recipes are also discussed.

Decreasing the Amount of Plasticizer and/or Emulsifier

Emulsions containing 10 percent of either Flexol TWS,[2/] Glyceryl Monoricinoleate S-1153 or Aroclor 1242 as plasticizer, 5 percent of Triton X-100 as emulsifier, and 1 or 2 percent of concentrated ammonium hydroxide were used as controls. The Glyceryl Monoricinoleate and Aroclor emulsions contained in addition 1 percent of Alkanol S. In the experimental emulsions, the amount of plasticizer was decreased to 5 percent or the amount of emulsifier to 2.5 percent, or both. All the emulsions were made by the same inversion procedure described in the above-cited paper, except that because of mixing difficulties in those Aroclor emulsions with reduced quantities of plasticizer and/or emulsifier, the water was added at 60° instead of 40° C. Stability observations were made after 1, 3, and 14 days, 1 month, and 2 months. Films were applied with a 4-mil Doctor-blade on plate glass, and the time required for them to become hard to the thumb and hard to the fingernail was determined. A month after the films were applied, the thickness and Sward Number of each were also obtained. Hardness was tested after 1, 3, 5, 7, and 10 days, 2 weeks, and 1 month. A film was considered hard to the thumb if it could not be blurred by rotating the thumb on it and at the same time applying as much pressure as possible between thumb and forefinger. A film was considered hard to the fingernail if it could not be dented, or if it could be only slightly scratched, with considerable difficulty.

The results are shown in Table I. Reducing the amount of emulsifier produced an improvement in hardness of the film of an Aroclor-plasticized emulsion only. It decreased the stability of a Flexol-containing emulsion. In all cases, however, reducing the amount of plasticizer produced some improvement. Reducing both plasticizer and emulsifier gave the highest Sward numbers in the films from the Glyceryl Monoricinoleate emulsions, but the emulsions were difficult to prepare and had less stability. Decreasing both

1/ Paint, Oil and Chemical Review, 114, 40-41, Oct. 11, 1951.

2/ Mention of commercial products does not imply that they are endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned.

Aroclor and emulsifier gave films of poor clarity. An attempt to decrease both Flexol and emulsifier yielded an unstable emulsion. Aroclor imparted greater initial hardness than the other plasticizers. Omitting the plasticizer and using additional emulsifier appeared to have some plasticizing or solubilizing effect. This formulation, however, appeared to have little or no advantage.

(Insert 1)

Addition of Polymerization Catalysts

Cobalt octoate, acetate and chloride were tried as catalysts for the polymerization of allyl starch in emulsion films, but they produced too much instability, either because of the presence of polyvalent ions or (in the octoate) because of a tendency to produce water-in-oil emulsions. For this reason, various cobalt complexes, all but the first supplied by Dr. T. P. McCutcheon of the University of Pennsylvania, were tried. These are listed below:

1. Composition unknown, obtained from General Mills, Inc.
2. Hexammino cobaltinitrate
3. Chlor pentammino cobaltichloride
4. Dinitro tetrammino cobaltichloride
5. Ammonium tetranitro diammino cobaltiate
6. Trinitro ammino ethylenediamine cobalt
7. Trinitro triammino cobalt
8. Dichlorodiethylenediamine cobaltichloride

The complexes were added to emulsions containing 10 percent plasticizer and 5 percent emulsifier. Those soluble in water were added dissolved in the water used to prepare the emulsions; the others were mixed with the emulsions just before the water was added. Enough complex was taken to give 0.1 percent cobalt metal, based on the weight of the allyl starch-plasticizer blend. Complexes Nos. 2 and 3 gave unstable emulsions, probably because of the presence of polyvalent ions. Emulsions containing the other complexes were stable in most cases for more than 2 weeks and in some cases for more than 1 month. Table II gives these data.

All the complexes tested were effective in increasing the hardening rate of the films. Of the various combinations tried, complex No. 5 used in Glyceryl Monoricinoleate-containing emulsions was the best. The films became hard to the fingernail in 6 or 7 days, whereas the control films were not this hard in 1 month. For Flexol-plasticized emulsions, complex No. 6 gave the best results; for Aroclor-plasticized emulsions, complexes 1, 5 and 7 gave the best results.

Table 1 Effects of varying the amounts of plasticizer and emulsifier on hardness of films and stability of emulsions

Emulsion No.	Percent plasticizer	Percent emulsifier	Stability (months)	Hard-to-thumb time (days)	Hard-to-fingernail time (months)	Sward No. (after 1 month)
Flexol TWS						
107[1/]	15	5	>2	10	>1	24
119[1/]	15	5	>2	10	>1	10
150A[1/]	10	5	-	4	21 days	36
161[1/]	10	5	>1	6	1	27
110A	15	2.5	1	10	>1	24
111	5	5	>2	3	1	43
Glyceryl Monoricinoleate S-1153						
108[1/]	10	5	>2	7	>1	34
119A[1/]	10	5	1-2	4	>1	22
148[1/]	10	5	2	6	>1	29
111A	10	2.5	1.5	7	1	35
112	5	5	>2	4	>1	44
114B	5	2.5	1	1	1	45
117A	5	2.5	0.5-1	1	1(brittle)	45
Aroclor 1242						
124[1/]	10	5	>2	4	>1	32
163A[1/]	10	5	>1	2	>1	24
126A	10	2.5	>2	1	1	38
126	5	5	>2	1	1	42
127	5	2.5	2	1	>1	42
No plasticizer						
123	-	10	>2	3	>1	36

1/ Control

Table II. Effect of cobalt complexes on hardness of films and stability of emulsions

Emulsion No.	Complex No.	Stability (months)	Hard-to-thumb time (days)	Hard-to-fingernail time (days)	Sward No. (after 1 month)
Flexol TWS					
150A	Control	-	4	21	36
161	"	>1	6	30	27
153	1	0.5	3	14	37
163C	4	>1	7	18	27
152A	5	1-2	3	14	36
151	6	>2	4	10	39
152	7	0.1-0.5	3	18	36
Glyceryl Monoricinoleate S-1153					
108	Control	>2	7	>30	34
119A	"	1-2	4	>30	22
148	"	2	6	>30	29
146A	1	0.5-1	3	10	46
144	4	0.5-1	4	15-30	43
144A	5	0.5-1	3	7	48
155	5	<0.5	3	6	46
142	6	0.5-1	3	14	46
146	6	0.5-1	5	21	43
142A	7	0.5-1	3	10	48
145	8	<0.5	8	15-30	35
Aroclor 1242					
124	Control	>2	4	>30	32
163A	"	>1	2	>30	24
154	1	0.5	4	11	41
163B	4	>1	7	30	27
150	5	1-2	4	10	39
148A	6	>2	3	18	41
149	7	0.5-1	3	11	43

Since greater stability might be desired in some cases, an attempt was made to add complexes 1 and 5, in aqueous solution, to an already prepared allyl starch-Glyceryl Monoricinoleate emulsion to see whether such complexes could be added just before the emulsion is to be used. This would obviate any problem of instability. Number 1 caused some precipitation, but No. 5 did not. A film of the emulsion containing No. 5 became hard to the fingernail in 6 days, and after 1 month had a Sward No. of 45.

Viscosity Control

The viscosity of the emulsions was increased by decreasing the amount of plasticizer or increasing the amount of emulsifier. In Glyceryl Monoricinoleate-containing emulsions the viscosity was also increased by decreasing the amount of water present. Some reduction in water content would no doubt be possible for some of the other emulsions.

Use of a thickening agent in preparing an emulsion has generally led to accelerated creaming. It was found, however, that Acco Acrylic Polymer No. 201 (a "modified sodium polyacrylate") could be added to an already prepared emulsion. An amount equal to 1 percent of the water increased the viscosity of an allyl starch-Flexol emulsion from 12 to 140 centipoises.

Preparation of Larger Emulsion Batches

Emulsions were prepared in the flask with twice the quantities previously employed (1 pint vs. 1/2 pint). A 1-quart emulsion was prepared in a kneading machine (Readco Mixer). The procedure was the same as for the flask except that a nitrogen atmosphere was not maintained and slightly more ammonia was used. These emulsions were stable and gave fairly clear films.

New Types of Emulsions

In some emulsions, morpholine and ethanolamine were used in place of ammonia, which has a lower boiling point and is lost more rapidly during preparation and storage of the emulsion. These emulsions, however, were not promising from the standpoint of stability and film clarity.

An emulsion containing 10 percent Flexol TWS and made with a new emulsifier, Polyethylene Glycol 400 Mono Laurate, gave clear films and was stable for 1 to 2 months.

The dye, Calco Oil Red N-1700, was used to give transparent magenta films. It was blended with allyl starch and Flexol before the emulsifying agents and water were added. The procedure was otherwise similar to that used for the other emulsions.

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